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COMPLETE SPECIFICATION

Catalytic Removal of Nitrogen-Containing Compounds from Hydrocarbons using Hydrogen

We, CALIFORNIA RESEARCH CORPORATION, a corporation duly organized under the laws of the State of Delaware, United States of America, and having offices at 200 Bush Street, San Francisco 4, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to processes for the selective hydrogenative removal of nitrogen-containing compounds from hydrocarbon streams, sometimes hereinafter referred to as hydrodenitrication. In a particular embodiment, the invention is concerned with a catalytic process for the substantially complete removal of nitrogenous contaminants from distillable hydrocarbon oils to be used as feed stocks in subsequent catalytic conversion processes.

It has long been known that nitrogen compounds could be removed to some extent from petroleum hydrocarbons by conventional hydrofining processes. However, even in the case of relatively low boiling feed stocks, substantially complete nitrogen removal cannot be accomplished by conventional hydrofining without the use of rather severe conditions of temperature and pressure and a relatively low space velocity. In the hydrofining process the hydrocarbon oil is treated with hydrogen at elevated temperature and pressure in contact with various catalysts generally comprising Chromium and/or molybdenum oxide together with iron, cobalt, and/or nickel oxides on a porous oxide support, such as alumina or silica-alumina. Previous investigations into the effect of the metals content of the hydrofining catalysts on their activity have indicated that there is little to be gained by the use of metal contents above about 14%. For example, it is indicated in U.S. patent number 2,758,957 to K. Nozaki that increasing the total metals concentration above 15%, by weight is of little benefit, and that decreasing the nickel content

of a Ni-Mo catalyst to an atomic ratio of 1:3 increased the activity for hydrogenation.

The present invention is based upon the discovery that for the purpose of substantially completely removing contaminating nitrogen-containing compounds from distillable hydrocarbon oils to low residual nitrogen levels, catalysts containing large concentrations of both nickel and molybdenum are outstanding in their properties and are not the equivalent of the large group of catalytic materials disclosed in the prior art. Thus according to one aspect of the invention, there is provided a process for the substantially complete removal of contaminating nitrogen-containing compounds from a distillable hydrocarbon oil, which process comprises contacting said hydrocarbon oil together with from 500 to 10,000 SCF of H_2 /bbl at a temperature of from 500 to 850°F., a pressure of from 200 to 4000 psig, and a liquid hourly space velocity of from 0.2 to 10 with a sulfided nickel-molybdenum-alumina catalyst containing from 4 to 10% by weight of nickel and from 15.5 to 30% by weight of molybdenum, said catalyst having previously been contacted in the oxide form with a sulfiding gas to convert nickel and molybdenum oxides predominantly to sulfides.

According to another aspect of the invention, there is provided a novel hydrodenitrication catalyst for use in the foregoing process which catalyst consists essentially of nickel and molybdenum sulfides on a predominantly alumina support and contains from 4 to 10% by weight of nickel and from 18.9 to 30% by weight of molybdenum in a weight ratio of nickel to molybdenum in the range 0.2 to 0.5, which catalyst has been contacted in the oxide form with a sulfiding gas to convert nickel and molybdenum oxides predominantly to sulfides to obtain high selective activity for the hydrogenative removal of nitrogen-containing compounds from hydrocarbon streams.

There are several embodiments of this inven-

tion. In one embodiment the invention provides a process whereby more than 99.9% of the initial nitrogen content of hydrocarbon naphthas boiling up to about 450°F. may be readily removed using relatively mild conditions of temperature and pressure and/or high space velocities by contacting the naphtha at 500—700°F. together with excess hydrogen, at a pressure of 200—1000 p.s.i.g. and at a liquid hourly space velocity of 1—10. Also, more than 99.9% of the initial nitrogen content of nonrefractory hydrocarbon middle distillates boiling up to about 600°F. may be readily removed by contacting such a middle distillate at 550—750°F. together with excess hydrogen, at a pressure of 500—1500 p.s.i.g. and at a liquid hourly space velocity of 0.5—5. In many cases 99.9% or more of the nitrogen is removed. In another embodiment, the invention provides a process whereby more than 99.9% of the initial nitrogen content of highly refractory hydrocarbon gas oils boiling up to about 750°F. may be removed using convenient conditions of temperature and pressure and moderate space velocities, by contacting the gas oil at 650—800°F. together with excess hydrogen, at a pressure of 500—2500 p.s.i.g. and at a liquid hourly space velocity of 0.2—5, which degree of nitrogen removal was heretofore unattainable in a commercially practical process. In another embodiment the invention provides a process whereby more than 99% of the initial nitrogen content of refractory or high boiling hydrocarbon oils boiling up to about 860°F. may be removed using moderate conditions of temperature, pressure and space velocity by contacting the oil at a temperature of 600—800°F. together with excess hydrogen, at a pressure of 500—4000 p.s.i.g. and at a liquid hourly space velocity of 0.2—5, which degree of nitrogen removal was heretofore unattainable at economically feasible operating conditions. In still another embodiment the invention provides a process whereby more than 80% of the initial nitrogen content of heavy hydrocarbon distillates boiling up to about 1050°F. may be removed using relatively mild conditions of temperature, pressure and/or space velocity, by contacting said distillate at a temperature of 600—800°F., together with excess hydrogen, at a pressure of 500—4000 p.s.i.g. and at a liquid hourly space velocity of 0.2—10, which degree of purification was heretofore unattainable without the use of conditions resulting in substantial coke formation. In general, the invention provides a process for the removal of contaminating nitrogen-containing compounds from any hydrocarbon oil to a much lower residual nitrogen level than was heretofore possible and using less severe operating conditions.

The feed stocks which may be treated by the process of this invention are distillable hydrocarbon oils. By this is meant those non-residual hydrocarbon streams normally pro-

cessed in petroleum refineries, and including naphthas, kerosenes, straight run and cracked distillates, distillates derived from shale oil orilsonite deposits, light and heavy cycle oils, and gas oils. In short, the process is applied to predominantly liquid hydrocarbon streams having an initial boiling point above about 180°F. and an end point below about 1050°F.

Hydrocarbon oils contain varying amounts of nitrogen-containing compounds, ranging from several parts per million up to 1—3%, depending on the boiling range of the oil and the nature of the crude petroleum or other hydrocarbonaceous deposit from which it was derived. It is not uncommon to report both total nitrogen and basic nitrogen in analyzing hydrocarbon oils. As used herein, the term "nitrogen content" refers to total nitrogen, determined by Kjeldahl analysis, expressed in parts per million of nitrogen.

The removal of contaminating nitrogen-containing compounds from hydrocarbon distillates to very low residual levels is of particular value where the distillate is to be converted in a low temperature hydrocracking process. In the low temperature hydrocracking process a hydrocarbon distillate of low nitrogen content is contacted with certain dual function catalysts, such as cobalt or nickel sulfide on a silica-alumina cracking catalyst support, under controlled conditions of temperature, pressure, hydrogen throughput, and space velocity, to effect a substantial conversion of the feed to liquid products boiling below the initial boiling point of the feed and containing a high ratio of iso- to normal paraffins, with negligible coke production and only a very small production of light gaseous hydrocarbons. Such a process has been denoted by the proprietary name "Isocracking". Pretreatment of the feed to a low temperature hydrocracking process to reduce the nitrogen content to less than 10 ppm permits the use of lower operating temperatures (e.g., below 700°F.), extends the on-stream time, and results in a more favorable product distribution. More favorable results are obtained when the feed has a nitrogen content of only 1—2 ppm. Nitrogen contents below 1 ppm are considerably more advantageous.

A typical light cycle oil derived from a fluid catalytic cracking process had a gravity of 25.4° API, an initial boiling point of 415°F., an end point of 550°F., and an initial nitrogen content of 900 ppm. This material can be virtually quantitatively converted to gasoline boiling range hydrocarbons by low temperature hydrocracking provided the nitrogen content is first reduced to less than 10 ppm. The inability of conventional hydrofining catalysts to effect such a degree of nitrogen removal at ordinary processing conditions is shown by the data given in Table I. The light cycle oil was contacted with each of the catalysts described in Table I at 615—620°F., 800

psig, in the presence of 4000 SCF H₂/bbl, at a liquid hourly space velocity (LHSV) of 1.0 v/v/hr based on the light cycle oil feed.

TABLE I
Hydrofining of Light Cycle Oil

Catalyst	A	B	C	D	E
Wt. % Molybdenum	6.8	8.3	6.5	9.2	15.3
Wt. % Nickel	—	—	2.4	3.1	2.7
Wt. % Cobalt	2.7	2.7	0.3	—	—
Wt. % Metals, Total	9.5	11.0	9.2	12.3	18.0
Product:					
ppm Nitrogen	244	345	145	108	108
% Nitrogen Removal	73	62	84	88	88
Catalyst Relative Activity	1.00	0.75	1.4	1.5	1.5

Catalyst A is a commercially available hydrofining catalyst prepared by a method comprising solution impregnation of cobalt salt (followed by calcining to the oxide) on a coprecipitated molybdenum oxide-alumina support. Catalyst B and Catalyst C are other commercial hydrofining catalysts wherein the metals molybdenum, nickel, and/or cobalt are supported on alumina. Catalyst D is a nickel-molybdenum-alumina catalyst prepared by impregnating an alumina carrier with an aqueous solution of nickel nitrate, drying and calcining, and then impregnating with aqueous ammonium molybdate, drying and calcining. Catalyst E was prepared in the same manner as Catalyst D, but using more concentrated impregnating solutions to provide a total metals content greater than has been found exemplified in the hydrofining or denitrification art. It is apparent that this increase in metal content was of no benefit, as predicted by the prior art. All of the catalysts were sulfided to convert the metal oxides predominantly to metal sulfides prior to contacting with the light cycle oil.

Catalyst A, being intermediate in activity Catalysts B and C, has been assigned a relative activity for hydrodenitrification of 1.00 expressed on a space velocity basis. We have found that the hydrodenitrification reaction closely approximates a pseudo first-order rate reaction with respect to the fractional removal of the initial nitrogen content over the range of operating conditions utilized, i.e., $-\log(1-x) = kt$, where x is the per cent nitrogen removal expressed as a decimal, t is the contact time (inversely proportional to LHSV), and k is the reaction rate constant (proportional to

relative activity). From this it can be shown that to reduce the nitrogen content of the light cycle oil from the initial 900 ppm to less than 10 ppm would require the use of a catalyst having a relative activity of about 3.5 under the conditions of the above test. For the substantially complete hydrodenitrification of distillates having a greater initial nitrogen content or of a more refractory nature (with respect to ease of denitrification) than the light cycle oil, a catalyst having a relative activity of about 4 or better is required.

We have found that to obtain the high activities required for the substantially complete removal of nitrogen-containing compounds, in accordance with this invention, the catalyst must contain at least 15.5% molybdenum and must also contain at least 4% nickel. Specifically, the highly active catalysts utilized in the process of this invention have nickel contents in the range 4—10% by weight and molybdenum contents in the range 15.5—30% by weight. The catalysts may be conveniently prepared by impregnating an alumina support with nickel and molybdenum compounds convertible to the oxides by calcination to give the finished catalyst the desired metals content, calcining, and then sulfiding to convert the nickel and molybdenum oxides predominantly to the sulfides. Alternately, the catalyst may be prepared by procedures involving coprecipitation of nickel, molybdenum, and alumina components, or by a combination of coprecipitation of molybdenum and/or nickel with aluminum followed by further impregnation with one or both of the metals. Other methods of preparation will be readily apparent to those skilled in the art.

When the light cycle oil described previously, having a nitrogen content of 900 ppm, was contacted with the nickel-molybdenum-alumina catalysts of this invention under the

same operating conditions as were used in the previous test, the nitrogen was substantially completely removed, as shown in Table II.

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TABLE II

Hydrodenitritication of Light Cycle Oil

Catalyst	J	K	L	M	N	P
Wt. % Molybdenum	18.9	24.3	22.0	21.8	21.8	21.7
Wt. % Nickel	4.7	4.1	5.9	7.6	10.0	4.9
Wt. % Metals, Total	23.6	28.4	27.9	29.4	31.8	26.6
Product:						
ppm Nitrogen	4	4.5*	3	1.5	4*	6
% Nitrogen Removal	99.55	99.5	99.7	99.8	99.55	99.3
Catalyst Relative Activity	3.8	3.7	4.0	4.6	3.8	3.5

* Corrected value based on data at 570—575° F.

Indicated relative activity confirmed by companion test runs with Catalyst A at 570—575° F.

- As shown by the data of Table II, nickel-molybdenum-alumina catalysts containing 4 to 10% Ni together with from 18.9 to 25% Mo are remarkably active with respect to hydrodenitritication, a fact which could not be predicted from a consideration of the catalysts containing lesser quantities of the metals. The molybdenum content may be as high as 30%. In all cases the molybdenum is in substantial atomic excess of the nickel, or expressed otherwise, the relative proportions are such that the weight ratio of nickel to molybdenum is less than 0.6. The highest activity appears to be obtained at weight ratios of nickel to molybdenum in the range 0.2—0.5, especially 0.25—0.4. Accordingly, the use of catalysts having nickel and molybdenum contents in the latter relative proportions is preferred, particularly 6—8% Ni with 21—23% Mo.

- It will be observed that to determine the per cent nitrogen removal required the accurate measurement of residual nitrogen concentrations of less than 10 ppm. The analyses were made in a "nitrogen-free" laboratory, set aside for the purpose, by a modified Kjeldahl procedure involving the extraction of a fairly large sample (100 gm) with 92% sulfuric acid. Highly purified water and caustic must be used, and all glassware should be cleaned with hot caustic. At the 1 ppm level the analyses are considered accurate to ± 0.1 ppm.

- Catalysts J, K, L, M, N and P were prepared by substantially the same procedure in order to insure that the results would be indica-

tive solely of the effect of the metals content. Catalysts D and E of Table I were prepared in this same manner, namely, alternate impregnation of alumina with aqueous solutions of nickel and molybdenum compounds convertible to the oxides by calcination. The procedure is exemplified by the preparation of Catalyst M, described in the following example. Unless otherwise stated parts and percentages are by weight.

EXAMPLE 1

A high grade alumina, obtained commercially in the form of $\frac{1}{16}$ " extrusions, having a pore volume of 0.65 cc/gm and a surface area by nitrogen adsorption of 270 M²/gm (B.E.T. method), was immersed for 2 hours at room temperature in an aqueous solution of nickel nitrate, prepared by adding 2 parts by weight Ni(NO₃)₂·6H₂O to 1.5 parts H₂O. The pH was about 5.2. The impregnated particles were dried for 10 hours at 400°F., and then calcined for 4 hours at 900°F. The calcined particles were then immersed for 2 hours in an aqueous solution of ammonium molybdate, prepared by mixing 3.9 parts of 20% NH₄OH, 3.2 parts of H₂O, and 2.9 parts of MoO₃, by weight. The pH was maintained at about 8.8 by the addition of more ammonium hydroxide solution. The impregnated particles were dried for 10 hours at 400°F., and then calcined for 4 hours at 900°F. The catalyst was then given a second molybdenum impregnation in the same manner, dried, and calcined as before. The nickel oxide-molybdenum oxide-alumina catalyst so pro-

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duced contained 7.6% Ni and 21.8% Mo, calculated as the metals, and had a surface area of 119 M²/gm. The oxide catalyst was then placed in a test reactor, and hydrogen was passed therethrough for about 1 hour, while raising the temperature to 650°F., at a pressure of 800 psig. A vaporized solution of dimethyldisulfide in heptane was added to the H₂ and fed to the reactor for a ten-hour period, at which time approximately 2.8 times the amount of sulfur required to convert the NiO and MoO₃ to Ni₃S₂ and MoS₂ had been introduced. The ratio of dimethyldisulfide to hydrogen was about 1 to 12, by volume, at the reactor inlet. The final catalyst had a relative activity of 4.6.

The above order of impregnation, namely, first nickel and then molybdenum, is preferred. When the reverse order was used, there was a tendency for molybdenum to be leached out of the catalyst during the second (nickel) impregnation. In addition, somewhat higher activities are obtained by following the preferred order of impregnation. Catalyst P was prepared by the reverse order of impregnation, as described in the following example.

EXAMPLE 2

Two hundred and fifty cc of alumina, obtained commercially in the form of 8—14 mesh pieces, having a pore volume of 0.49 cc/gm and a surface area by nitrogen absorption of 180 M²/gm, was immersed for 24 hours at room temperature in a solution of ammonium paramolybdate, prepared by adding to 94.6 gms of (NH₄)₆Mo₇O₂₄·4H₂O sufficient water to make up 200 ml of solution. The impregnated alumina was then drained free of excess solution, dried for 24 hours at 250°F., and calcined for 6 hours at 900°F. This material was then vacuum impregnated with molybdenum using an ammonium paramolybdate solution of the same molybdenum content as in the first impregnation, to which 0.2 cc of concentrated ammonium hydroxide had been added per gram of ammonium molybdate. The once-impregnated alumina was placed in a flask, the flask evacuated, and 200 ml of the ammonium molybdate solution was introduced. The vacuum was released, and the mixture was allowed to stand for 15 minutes at atmospheric temperature and pressure. After drying and calcining as before, this material was given a third molybdenum impregnation in the same manner as the second impregnation. After drying and calcining as before, the alumina-molybdenum oxide catalyst was vacuum impregnated with nickel, in the same manner, using a solution prepared by adding to 319 grams of Ni(NO₃)₂·6H₂O sufficient water to make up 200 ml of solution. The four-times impregnated catalyst was then dried at 250°F. for 24 hours and calcined at 900°F. for 6 hours. The nickel oxide-molybdenum oxide-alumina catalyst so produced contained 4.9%

Ni and 21.7% Mo, calculated as the metals, and had a surface area of 93 M²/gm. The oxide catalyst was then sulfided with dimethyldisulfide in the same manner as in Example 1. The final catalyst had a relative activity of 3.5.

To obtain high activity for the hydrodenitrication process the high metals content nickel oxide-molybdenum oxide-alumina catalysts must be sulfided prior to contacting with the hydrocarbon oils to be treated. Sulfiding is preferably accomplished in the manner described in Example 1, by passing over the oxide catalyst a sulfiding agent such as H₂S, CS₂, a mercaptan or a disulfide. When H₂S is used, the sulfiding may be effected with or without a carrier gas such as hydrogen or nitrogen. High activity catalysts, comparable to those described in Table II, have been prepared by sulfiding directly with pure H₂S. Where sulfur compounds other than H₂S are employed, hydrogen should also be present, preferably under pressure, and the temperature should be sufficiently elevated for ready conversion of the sulfur compound to H₂S, say about 400°F. in the case of mercaptans and disulfides. Extensive reduction of the oxides to the metals is preferably avoided, since usually more active catalysts result if the oxides are sulfided directly. Further, to minimize reduction of the oxides, the temperature during sulfiding preferably should not exceed 750°F., and more preferably is at or below 650°F.

In a preferred method of sulfiding, mercaptan or organic disulfide addition is continued over a period of about 2—10 hours until at least 1.5 times the theoretical amount of sulfur required to convert the nickel and molybdenum oxides to Ni₃S₂ and MoS₂, respectively, has been added. The exact form of the metals in the final catalyst is not known, and it is not meant to represent that the nickel and molybdenum are quantitatively converted to Ni₃S₂ and MoS₂. However, it is important that an excess of the sulfiding agent be used in order to insure conversion of the metal oxides predominantly to the sulfides. When the oxide catalysts of this invention are contacted directly with the hydrocarbon oil and hydrogen at or slightly below the normal operating temperatures, relying on the inherent sulfur content of the hydrocarbon oil to effect sulfiding, the hydrodenitrication activity is only slightly better than that of the catalysts described in Table I.

When the catalyst is prepared by the successive impregnation method, the preferred catalyst support is substantially a microporous alumina, such as is commercially available or may be prepared by well known methods. The inclusion in the support of a small amount of silica, say up to 5%, would not be expected to affect the catalyst activity materially, and may be advantageous in stabilizing the catalyst in some cases. Highly active catalysts have also

been prepared by impregnating a coprecipitated molybdenum oxide-alumina hydroforming catalyst with nickel and additional molybdenum to provide metal concentrations in the required range. Alumina base hydrofining catalysts of conventional molybdenum and cobalt content may also be utilized as the support if the area and pore volume are adequate. Cobalt cannot be substituted for nickel, as cobalt-molybdenum catalysts containing 4–10% cobalt and 15.5–30% molybdenum are only about half as active for denitrification as the corresponding nickel-molybdenum catalysts. However, the inclusion of a small amount of cobalt in the catalyst in addition to the 4–10% nickel does not materially affect the basic and novel characteristics of the catalyst for denitrification, nor does the inclusion of minor amounts of zinc or copper. The inclusion of such metals appears to be somewhat deleterious, and they are preferably excluded. The support should be predominantly alumina.

To permit the required incorporation in the alumina carrier of more than 19% by weight of the metals, nickel and molybdenum, without substantially filling the pores, the alumina should have an initial pore volume in excess of about 0.2 cc/gm. It is preferred that the alumina have a pore volume of greater than about 0.4 cc/gm. Since the impregnation with large quantities of nickel and molybdenum results in a reduction of the surface area, it is desirable to start with a carrier having a surface area in excess of about 150 M²/gm, as determined by nitrogen adsorption; although the surface area may be as low as 75 M²/gm if, for example, the catalyst is to contain only 4–5% Ni and 15.5–19% Mo. The alumina may be calcined if desired prior to impregnation with the metals, but precalcining does not appear to be essential except as a means of increasing the pore volume and structural strength of the support.

Where the catalyst is to be employed in a fixed bed process, the alumina is preformed, as in the shape of small spheres, pellets, rods, or irregular pieces. In the impregnation method of preparation, preferably a preformed alumina carrier is first immersed in an aqueous solution of a nickel compound readily convertible to the oxide by calcination, such as nickel nitrate or nickel acetate. Nickel sulfate is a less desirable impregnating compound, and nickel chloride is even less desirable, because of the high temperatures required for decomposition or conversion to the oxide. The preferred medium is an aqueous solution of nickel nitrate containing 2–12% Ni, depending on the final nickel concentration desired in the catalyst. The impregnated carrier is then dried and calcined or otherwise treated to convert the nickel compound to nickel oxide.

The nickel oxide-alumina catalyst is then impregnated with an aqueous solution of a molybdenum compound convertible to the

oxide by calcination, such as ammonium molybdate, or a solution of molybdic acid in an oxalic acid solution containing nitric acid. When ammonium molybdate is used, the pH should be controlled at above about 7.7 to prevent precipitation of molybdenum oxide. Preferably, the pH is maintained at about 8.7 or above to avoid the formation of a molybdenum oxide crust on the outer surface of the catalyst. The twice-impregnated catalyst is then dried and calcined. This catalyst can then be given an additional molybdenum impregnation, again followed by drying and calcining, when it is desired to prepare a catalyst containing above 16% molybdenum. However, molybdenum contents up to about 19% by weight in the finished catalyst have been obtained by a single impregnation with ammonium molybdate.

The final calcination is effected at temperatures in the range 600–1100°F. When a high nickel and molybdenum content catalyst was calcined at or slightly above 1200°F., the relative activity for hydrodenitrification was approximately halved. Thus, when the nickel is incorporated after the molybdenum, the nickel compound used should be one convertible to the oxide at a temperature below 1200°F. The optimum calcining temperature appears to be between 800°F. and 1000°F. The calcinations are usually carried out in the presence of hot air, but an inert gas atmosphere may instead be used since oxygen is already available in the preferred impregnating compounds.

Suitable catalysts can also be prepared by simultaneously coprecipitating the nickel, molybdenum, and aluminum components. Coprecipitation is sometimes preferred, particularly for preparing catalysts with the metal contents in the higher end of the range. In the coprecipitation method of preparation, preferably an aqueous solution of a basic molybdenum salt, such as an ammoniacal ammonium molybdate solution, and an aqueous solution of acidic salts of nickel and aluminum, such as the chlorides, acetates, or nitrates, are poured slowly into a third aqueous solution with vigorous mixing. The solution compositions and rates of addition are preferably controlled such that a pH near neutrality is maintained in the mixture to obtain a more uniform coprecipitate. The resultant gelatinous coprecipitate of nickel, molybdenum, and aluminum oxides and/or hydroxides is filtered and washed repeatedly to remove the soluble acid-base salts also formed. The coprecipitate is then dried slowly to remove residual moisture and to form an alumina gel structure, after which it is calcined to form a nickel oxide-molybdenum oxide-alumina catalyst. The calcined oxide catalyst is then sulfided, in the same manner as heretofore described in the case of the catalysts prepared by impregnation, to convert nickel and molybdenum oxides predominantly

to the sulfides. Best results were obtained when the aforementioned third aqueous solution was a dilute solution of a high molecular weight organic material, such as animal glue, and the precipitation was accomplished at a pH of 6—7. A catalyst prepared in the above-described manner, containing 8.2% nickel and 29.8% molybdenum, had a relative activity as compared to Catalyst A of 4.0.

In another similar catalyst preparation method molybdenum and aluminum components are coprecipitated in the above-described manner, for example, by pouring together an ammoniacal ammonium molybdate solution and an aluminum chloride solution. The resulting coprecipitate is washed thoroughly to remove ammonium chloride, dried to remove residual moisture, and calcined to form a molybdenum oxide-alumina composite. This material is then impregnated with nickel nitrate, dried, calcined, and sulfided. A catalyst prepared in this manner, containing 7% nickel and 30% molybdenum, had a relative activity of about 5. In another catalyst preparation molybdenum and aluminum components were coprecipitated in the above manner but with the solution strength adjusted to give a lower molybdenum content. The calcined composite was then further impregnated with nickel nitrate and with additional ammonium molybdate. The finished catalyst contained 4.9% nickel and 15.6% molybdenum, and had a relative activity of about 5. Catalysts can also be prepared by coprecipitation of nickel and molybdenum on a calcined alumina or a hydrous alumina gel. In all cases, the calcination and sulfiding steps are preferably carried out under the same conditions and in the same manner as in the case of the previously described impregnation method of preparation.

Although the hydrodenitrification process may be carried out in a number of ways, such as by maintaining the catalyst in a fluidized bed or as a downflowing column of granular solids, the process is most suitably carried out using a fixed bed of catalyst in the manner depicted in the accompanying drawing. Of course, several catalyst beds may be used, with parallel and/or series flow of hydrocarbon, upflow or downflow, concurrent or countercurrent to H_2 . In many cases it is advantageous to use two beds in series with removal of NH_3 from the effluent of the first prior to passing that effluent to the second bed. Since the nickel-molybdenum catalysts of this invention maintain their high activity over protracted periods of use, a continuous non-regenerative type of operation is obtainable and is normally preferred. The catalysts may be regenerated periodically by the oxidative removal of carbon deposits formed during extended use.

Referring to the accompanying drawing, the hydrocarbon oil to be treated enters the process

via line 1. Hydrogen-rich gas is admixed with the hydrocarbon oil feed via line 2, and the admixture, after heating to the desired operating temperature, passes to reactor 4 via line 3. Alternately, the hydrocarbon and hydrogen streams may be separately heated before mixing. Reactor 4 is packed with sulfided high metals content nickel-molybdenum-alumina catalyst in the form of small particles such as spheres, pellets, or extrudates. The hydrocarbon oil feed may be completely vaporized in the case of low boiling feed stocks, but mixed phase flow is preferred in the case of higher boiling stocks. In passing through reactor 4 the nitrogen-containing compounds in the hydrocarbon oil are substantially converted to ammonia with concomitant consumption of hydrogen. The reactor effluent leaves via line 5, and is cooled to condense the normally-liquid hydrocarbon portion and then passed via line 7 to separation drum 8. To assist in the removal of ammonia from the effluent, water or acidulated water may be added through line 6. A water phase containing dissolved NH_3 , which then separates in drum 8 may be withdrawn via line 14 and discarded. A major portion of the ammonia formed may be removed in this fashion.

Hydrogen-rich recycle gas is separated in drum 8 and withdrawn through line 9 to compressor 10, for return to the reaction zone in combination with additional feed via lines 11 and 2. Make-up hydrogen is introduced through line 13 to compensate for that consumed in the process. It may be desirable to withdraw a small bleed stream of recycle gas via line 12 to limit the build-up in the recycle stream of light gaseous hydrocarbons, such as may be introduced with the make-up hydrogen.

Liquid hydrocarbon effluent, containing residual ammonia and other hydrogenated impurities, is withdrawn from drum 8 and passed to distillation zone 16 via line 15. Zone 16 is operated at a materially lower pressure than drum 8, and may comprise another simple separation drum, or it may be a stripping column, as shown. Steam, hydrogen, or other inert stripping gas is introduced via line 17 to assist in the complete removal of ammonia and other light gaseous by-products overhead via line 19. Purified hydrocarbon oil substantially free of nitrogen compounds is recovered in line 18. Alternately, or in addition to water washing and/or distillation, equivalent means for removing the NH_3 may be provided, for example, by adsorption on a microporous metal-alumino-silicate (molecular sieve), or activated earth.

Conditions of temperature, pressure, hydrogen throughput, and space velocity in the reactor are correlated to provide the desired degree of nitrogen removal. Higher temperatures, pressures, and/or hydrogen throughputs are required when treating the higher boiling

feed stocks and those containing the more refractory nitrogen compounds. A particular advantage of the process is that it permits the hydrodenitritication of refractory stocks at comparatively mild conditions of temperature and pressure and/or the use of high space velocities. The term "refractory" is used herein with reference to the relative difficulty with which nitrogen is removed from the respective feed stocks. In general, the complex nitrogen-containing compounds found in high boiling hydrocarbon fractions and cracked cycle oils are more resistant to hydrogenation than those found in the lower boiling hydrocarbon fractions and straight-run distillates.

Temperature has a large influence on the rate of conversion of the nitrogen-containing compounds and is adjusted upwards to maintain the hydrodenitritication rate as the catalyst ages or is deactivated through protracted use. The temperature must be in the range 500—850°F., preferably 600—750°F. The rate of hydrodenitritication is fairly low at temperatures below 550°F. At temperatures above 800°F. coke formation tends to increase markedly. With less active catalysts than those of the present invention the temperature at the start of the run must be much higher, and the on-stream time between catalyst regenerations is correspondingly reduced. The active hydrodenitritication catalysts of the present invention make possible the use of temperatures

at the lower end of the operating range for long periods of time. Hence, a special feature of this invention is the relatively low temperature of operation and the resultant long catalyst life.

Elevated pressures advantageously influence the rate of hydrodenitritication as well as extending the catalyst activity and life. Pressures as low as 200 psig may be employed when treating light naphthas, whereas pressures up to 4000 psig may be advisable for the substantially complete hydrodenitritication of highly refractory and high boiling stocks. Using the highly active catalysts of this invention the pressure will generally be in the range 200—2500 psig.

Hydrogen throughput rate is maintained above 500 SCF/bbl. More generally, at least sufficient hydrogen is provided to supply that consumed in the conversion of the nitrogen-containing compounds and to compensate for incidental hydrogenation of unsaturates and oxygen, sulfur, and halogen compounds, while maintaining a significant excess of hydrogen partial pressure. The use of more than 10,000 SCF of H₂/bbl does not generally produce sufficient improvement in conversion rate to justify the increased cost.

Table III presents physical inspection data on several typical distillable hydrocarbon oils which have been treated by the process of this invention for the substantially complete removal of nitrogen compounds.

TABLE III

Hydrocarbon Oil	Boiling Range					Gravity °API	Initial ppmN(Total)
	IBP	5%	50%	95%	EP		
Cracked Naphtha	274	291	331	402	419	44.8	220
FCC Light Cycle Oil	415	451	480	523	550	25.4	900
Coker Distillate	380	447	507	582	605	24.8	2500
Arabian Gas Oil	585	626	671	714	723	29.1	462
Heavy Cycle Oil	565	631	704	790	840	22.6	566
Heavy Gas Oil	513	602	718	818	862	19.5	2500
		14%	78%				
Cat Cracker Feed	385	625	925		1045	20.6	4000

Tables IV—VII, hereinafter, list typical and preferred ranges of operating conditions which are used in the practice of this invention for the hydrodenitritication of the various types of distillates exemplified in Table III. The typical conditions shown are selected for the hydrodenitritication of the particular stocks of Table III. The conditions used in a given case with

other, but similar, distillates will differ somewhat depending on the source and prior treatment of the particular distillate, the initial nitrogen content, and the degree of purification desired. Since the operating conditions of temperature, space velocity, and pressure are interrelated in their effect on the rate of hydrodenitritication, the appropriate conditions

in a given case are selected from the preferred ranges with reference to the typical operating conditions shown. Thus, to obtain a greater or lesser degree of nitrogen removal than the typical values shown, a higher or lower temperature or pressure, or a lower or higher space velocity, respectively, are selected from the preferred range. Similarly, if it is desired to use a higher space velocity for the same degree of purification, a higher temperature and/or pressure is selected. As a guide or first approximation to the relationship between these variables, it may be stated that doubling the space velocity usually has about the same effect on the relative completeness of nitrogen removal as decreasing the temperature by about 50°F. or reducing the pressure 30—50%.

The cracked naphtha and the light cycle oil of Table III are examples of relatively non-refractory hydrocarbon oils. The removal of more than 99.9% of the initial nitrogen con-

tent from such distillates is readily accomplished by the hydrodenitritication process according to the invention. For example, Table IV below presents typical and preferred operating conditions which can be used to reduce the nitrogen content of these and similar stocks to less than 1 ppm using the preferred high nickel and molybdenum content catalysts, having relative activities of about 4 or better. Using the highly active catalysts disclosed herein, containing 4—10% Ni and 15.5—30% Mo, feed stocks for low temperature hydrocracking containing less than about 1 ppm nitrogen can be prepared from non-refractory hydrocarbon distillates similar to the cracked naphtha and light cycle oil, boiling up to about 600°F. and having initial nitrogen contents up to about 10,000 ppm, by hydrodenitritication under the indicated preferred operating conditions.

TABLE IV
Hydrodenitritication of Non-Refractory Oils

	Operating Conditions	
	Typical	Preferred Range
Feed	Cracked Naphtha	<450° F. E.P. Naphthas
Initial ppm N	220	<10,000 ppm
Final ppm N	0.1	<1
% Nitrogen Removal	99.95	99.9—99.99+
Temperature, °F.	575—585	500—700
Pressure, psig	800	200—1000
H ₂ Throughput, SCF/bbl	4000	500—5000
Space Velocity, LHSV	2	1—10
Feed	Light Cycle Oil	<600° F. E.P. Middle Distillates
Initial ppm N	900	<10,000 ppm
Final ppm N	1	<1
% Nitrogen Removal	99.9	99.9—99.99
Temperature °F.	625—635	550—750
Pressure, psig	800	500—1500
H ₂ Throughput, SCF/bbl	4000	1000—10,000
Space Velocity, LHSV	1	0.5—5

When the cracked naphtha is contacted with the hydrofining catalyst (Catalyst A, as described above) at 800 psig, 4000 SCF H₂/bbl, and 2 LHSV, the temperature must be raised to above 650°F. to obtain the same degree of nitrogen removal. At 650°F. a space velocity of about 8 or better can be used with the active catalysts of this invention. Thus, a particular advantage of the invention is that it permits the use of high space velocities in treating light hydrocarbons. Similarly, using Catalyst A to treat the light cycle oil at 800 psig, 4000 SCF H₂/bbl, and 1 LHSV, the temperature must be raised to above 750°F. to obtain the indicated degree of nitrogen removal.

The coker distillate and the Arabian gas

oil of Table III are highly refractory stocks, and they require more severe conditions to effect the removal of more than 99.9% of the nitrogen-containing compounds. Table V presents typical and preferred operating conditions which can be employed to reduce the nitrogen content of these stocks to 1 ppm or less when using the high nickel and molybdenum content catalysts of this invention. Feed stocks for low temperature hydrocracking, containing less than 10 ppm nitrogen, can be prepared from such refractory distillates, boiling up to about 750°F. and having initial nitrogen contents up to about 10,000 ppm, by hydrodenitritication under the indicated preferred operating conditions.

TABLE V

Hydrodenitritication of Refractory Oils

	Operating Conditions		
	Typical	Typical	Preferred Range
Feed	Coker Distillate	Arabian Gas Oil	<750° F. E.P. Gas Oil Distillates
Initial ppm N	2500	462	<10,000
Final ppm N	1	0.5	<10
% Nitrogen Removal	99.96	99.9	99—99.99
Temperature, °F.	700—715	685—700	650—800
Pressure, psig	1200	1200	500—2500
H ₂ Throughput, SCF/bbl	6500	6000	1000—10,000
Space Velocity, LHSV	0.5	0.5	0.2—5

When the coker distillate or the Arabian gas oil are contacted with the hydrofining catalyst (Catalyst A) at 1200 psig, 6000—6500 SCF H₂/bbl, and 0.5 LHSV, the temperature must be raised to above 850°F. to obtain the indicated typical nitrogen removal. At such high temperatures the catalyst is rapidly deactivated by coke formation.

Hydrocarbon distillates such as the cracked naphtha, light cycle oil, coker distillate, and Arabian gas oil, after substantially complete removal of the contaminating nitrogen-containing compounds, are particularly good feed stocks for the low temperature hydrocracking process. In that process the purified oil is contacted at 350—750°F., 500—3000 psia H₂ partial pressure 0.3—5 LHSV, and in the presence of 2000—15,000 SCF H₂/bbl with a low temperature hydrocracking catalyst. The advantages gained by pretreatment of such

hydrocarbon oils in accordance with this invention are illustrated by the following example:

EXAMPLE 3

The FCC light cycle oil of Table III was contacted at 620°F., 800 psig, in the presence of 4000 SCF H₂/bbl, and at a space velocity of 1 LHSV with Catalyst M, prepared as described in Example 1, comprising 7.6% Ni and 21.8% Mo (calculated as the metals) supported on alumina and sulfided with dimethyldisulfide. After water washing and distilling to remove NH₃, the product oil analyzed 1.5 ppm nitrogen (total). When the temperature was raised to 650°F. the product analyzed only 0.1 ppm nitrogen. Under the latter higher temperature conditions the product contained 100 ppm nitrogen when the conventional hydrofining catalyst (Catalyst A) was used. When the light cycle oil containing 1.5 ppm nitrogen is

contacted with a low temperature hydrocracking catalyst, comprising 6% nickel sulfide supported on a silica-alumina cracking catalyst, the hydrocracking process may be initiated at 570°F., 1500 psig, 8000 SCF H₂/bbl, and 1.0 LHSV, and 60% conversion per pass may be maintained for over 2500 hours by gradually raising the hydrocracking reactor temperature to 715°F. When the feed contains only 0.1 ppm nitrogen, the same conversion may be maintained for over 4000 hours before a temperature of 715°F. is reached. But, if 100 ppm nitrogen were present in the feed, the temperature would have to be raised to above 700°F. very early in the run, and the hydrocracking run length (terminated at 715°F.) would be reduced to less than 100 hours.

In the treatment of high boiling stocks such

as the heavy cycle oil, heavy gas oil, and cat cracker feed described in Table III, a broad range of conditions may be used depending on the degree of nitrogen removal desired and the use to which the stock is to be put. Table VI presents typical and preferred operating conditions which can be employed to remove more than 99% of the nitrogen from the heavy cycle oil and heavy gas oil using the preferred catalysts of this invention. As shown in Table VI, the nitrogen content of such high boiling oils, boiling up to about 860°F. and having an initial nitrogen content below about 10,000 ppm., can be sufficiently reduced by this process to less than 10 ppm. of nitrogen, such that these and similar stocks may also be used as feedstocks to a low temperature hydrocracking process.

TABLE VI
Hydrodenitrification of High Boiling Oils

Feed	Operating Conditions		
	Typical Heavy Cycle Oil	Typical Heavy Gas Oil	Preferred Range <860° F. E.P. Gas Oils
Initial ppm N	566	2500	<10,000
Final ppm N	1	10	<10
% Nitrogen Removal	99.8	99.6	99—99.9
Temperature, °F.	660—675	735—750	600—800
Pressure, psig	1200	1600	500—4000
H ₂ Throughput, SCF/bbl	4100	4000	1000—10,000
Space Velocity, LHSV	0.5	0.5	0.2—5

As shown in Table VI the substantially complete hydrodenitrification of refractory and high boiling oils, such as the heavy gas oil, requires rather severe conditions even when using the high metal content catalysts. On the other hand, such a degree of nitrogen removal is incapable of being accomplished at economically feasible operating conditions using the hydrofining catalysts. For example, to obtain the indicated 99.6% nitrogen removal from the heavy gas oil with Catalyst A at 1600 psig, 4000 SCF H₂/bbl, and 0.5 LHSV, requires the use of a temperature in excess of 900°F. Similarly, to obtain the indicated degree of nitrogen removal from the heavy cycle oil at 1200 psig, 4000 SCF H₂/bbl and 0.5 LHSV with Catalyst A, requires the use of a temperature above 800°F.

Although the hydrodenitrification process is of particular value for use in the preparation of a feed stock for low temperature hydrocracking, improved operation and product distribution are also obtained in isomerization, hydrogenation, reforming, catalytic cracking, and like processes when the feed is first pretreated to remove nitrogen. In particular, we have found that isomerization catalysts, especially the solid acid or the dual function type, are rapidly poisoned by basic nitrogen compounds. The ability to remove the nitrogen-containing compounds normally present in hydrocarbon oils makes possible a wide variety of processes for the upgrading of inferior stocks. Thus, high quality jet fuel of low freezing point may be prepared by a process wherein a kerosene boiling range distillate of

appreciable n-paraffin content, normally unsuited for jet fuel usage, is first treated for the removal of nitrogen-containing compounds in accordance with the process of this invention.

5 The purified oil is then contacted with an isomerization catalyst, such as halided platinum-on-alumina or nickel-molybdenum on silica-alumina, at 300—700°F., 100—2000 psig, at a liquid hourly space velocity of from about 0.1 to 5, and in the presence of added hydrogen. Similarly, lubricating oils of low pour point and high viscosity index may be produced by hydrodenitrification of crude wax or wax-bearing distillates and lubricating oils in the manner set forth herein, followed by isomerization at elevated pressure and temperature, in the range 400—800°F., and at a liquid hourly space velocity of from about 0.01 to 4, in contact with a catalyst such as the aforementioned platinum-alumina type or, for example, comprising alumina on which is deposited vanadium or tungsten together with molybdenum, cobalt, or nickel.

For many purposes a lesser degree of nitrogen removal is of considerable value provided that relatively moderate processing conditions can be used. For example, it has been found that when a heavy gas oil, similar to the heavy gas oil of Table III, with its nitrogen content reduced to 100 ppm is fed to a catalytic cracking pilot unit operating at 900°F., a space rate of 1.5 and a catalyst to oil ratio of 1:5, a total conversion of 51 volume per cent and a 37 volume per cent gasoline yield are obtained. At a nitrogen content of 2500 ppm the stock is only 33 volume per cent converted with a 25 volume per cent gasoline yield, at the same operating conditions. Table VII presents typical and preferred operating conditions which can be employed to remove the greater portion of the nitrogen contaminants from stocks such as the heavy gas oil and the full boiling range cat cracker feed of Table III using the high activity catalysts of this invention.

TABLE VII

Hydrodenitrification of Heavy Oils

Feed	Operating Conditions		
	Typical	Typical	Preferred Range
	Heavy Gas Oil	Cat Cracker Feed	<1050° F. E.P. Heavy Distillates
Initial ppm N	2500	4000	—
Final ppm N	100	750	—
% Nitrogen Removal	96	85	80 + %
Temperature, °F.	680—695	735—755	600—800
Pressure, psig	1600	2000	500—4000
H ₂ Throughput, SCF/bbl	4000	4000	1000—10,000
Space Velocity, LHSV	0.5	2	0.2—10

Under the indicated typical operating conditions of Table VII only about 50% of the nitrogen is removed when the hydrofining catalyst (Catalyst A) is used for treating either the heavy gas oil or the cat cracker feed.

In the foregoing comparisons, namely, Tables IV, V, VI and VII, it would appear that substantially complete hydrodenitrification could be accomplished using conventional hydrofining catalysts by resorting to operation at extremely low space velocities, for example, less than 0.2 LHSV. The use of such low space velocities is particularly undesirable in the treatment of hydrocarbon distillates not

only because of the greatly increased equipment and catalyst costs involved but also because of the necessarily increased time of contact with the catalyst at elevated temperature. Protracted exposure of distillable hydrocarbon oils to high temperatures and catalytic agents in many cases intensifies degenerative side reactions, notably thermal cracking and degradation of color and stability. In contrast thereto, for any desired degree of nitrogen removal the highly active, high nickel and molybdenum content catalysts permit the use of more moderate temperature conditions and higher space velocities. Under such compara-

tively mild conditions it has been found that many stocks may be substantially decolorized by the hydrodenitrification process. For example, the pretreatment of the light cycle oil under the conditions of Example 3 yielded a product which was essentially colorless (+15 Saybolt). Thus, it is contemplated that the utilization of the active nickel-molybdenum catalysts in the manner disclosed herein may provide a method whereby many stocks such as stove oils, lube oil fractions, transformer oils, waxes, and special products may be purified to an extent not heretofore considered possible.

15 WHAT WE CLAIM IS:—

1. A hydrodenitrification catalyst which consists essentially of nickel and molybdenum sulfides on a predominantly alumina support and contains from 4 to 10% by weight of nickel and from 18.9 to 30% by weight of molybdenum in a weight ratio of nickel to molybdenum in the range 0.2 to 0.5, which catalyst has been contacted in the oxide form with a sulfiding gas to convert nickel and molybdenum oxides predominantly to sulfides to obtain high selective activity for the hydrogenative removal of nitrogen-containing compounds from hydrocarbon streams.

2. A catalyst as claimed in Claim 1, said catalyst being prepared by co-precipitating nickel, molybdenum, and aluminium components by mixing an aqueous ammoniacal ammonium molybdate solution with an aqueous solution of acidic salts of nickel and aluminium at a pH near neutrality, filtering and washing the resulting co-precipitate to remove soluble ammonium salts, drying the washed co-precipitate, calcining the dried co-precipitate to form a nickel oxide-molybdenum oxide-alumina catalyst, and sulfiding the calcined co-precipitate to convert nickel and molybdenum oxides predominantly to the sulfides.

3. A catalyst as claimed in Claim 1, said catalyst being prepared by impregnating a predominantly alumina support successively with nickel and molybdenum compounds convertible to the oxides by calcination, calcining after each impregnation to convert the nickel and molybdenum compounds to the metal oxides, and sulfiding the impregnated and calcined catalyst to convert said metal oxides predominantly to metal sulfides.

4. A catalyst as claimed in Claim 1, said catalyst being prepared by coprecipitating molybdenum and aluminum components by mixing an aqueous ammoniacal ammonium molybdate solution with an aqueous solution of an acidic aluminum salt at a pH near neutrality, filtering and washing the resulting coprecipitate to remove soluble ammonium salts, drying the washed coprecipitate, and calcining the dried coprecipitate to form a molybdenum oxide-alumina composite, impregnating the calcined coprecipitate with a nickel compound convertible to the oxide by

calcination, calcining to form a nickel oxide-molybdenum oxide-alumina catalyst, and sulfiding the calcined catalyst to convert nickel and molybdenum oxides predominantly to the sulfides.

5. A hydrodenitrification catalyst substantially as described in Example 1 or 2 of the foregoing Examples.

6. A process for the substantially complete removal of contaminating nitrogen-containing compounds from a distillable hydrocarbon oil, which process comprises contacting said hydrocarbon oil together with from 500 to 10,000 SCF of H_2 /bbl at a temperature of from 500 to 850°F., a pressure of from 200 to 4000 psig, and a liquid hourly space velocity of from 0.2 to 10 with a sulfided nickel-molybdenum-alumina catalyst containing from 4 to 10% by weight of nickel and from 15.5 to 30% by weight of molybdenum, said catalyst having previously been contacted in the oxide form with a sulfiding gas to convert nickel and molybdenum oxides predominantly to sulfides.

7. A process according to Claim 6, wherein said sulfided catalyst contains from 6 to 8% by weight of nickel and from 21 to 23% by weight of molybdenum.

8. A process according to claim 6 or 7, wherein the process is carried out with the catalyst claimed in claim 2.

9. A process according to claim 6 or 7, wherein the process is carried out with the catalyst claimed in claim 3.

10. A process according to Claim 6 or 7, wherein the process is carried out with the catalyst claimed in claim 4.

11. A process according to Claim 6 for the removal of contaminating nitrogen-containing compounds from a hydrocarbon oil boiling below about 860°F. and having an initial nitrogen content below about 10,000 ppm, which process comprises passing said hydrocarbon oil together with hydrogen at elevated temperature and pressure through a fixed bed of the catalyst claimed in Claim 1 contained in a reactor, cooling the effluent vapors to condense the normally liquid hydrocarbons therein, separating from said liquid hydrocarbons at substantially the reactor pressure a recycle gas comprising hydrogen, removing ammonia from the said hydrocarbons, and recovering as the purified oil product a feedstock for a low temperature hydrocracking process containing less than 10 ppm nitrogen.

12. A process according to Claim 6 for the removal of more than 99.9% of the contaminating nitrogen-containing compounds from a hydrocarbon naphtha boiling up to about 450°F., which process comprises contacting said naphtha at 500 to 700°F. together with excess hydrogen at a pressure of 200 to 1000 psig and at a liquid hourly space velocity of 1 to 10.

13. A process according to Claim 6 for the

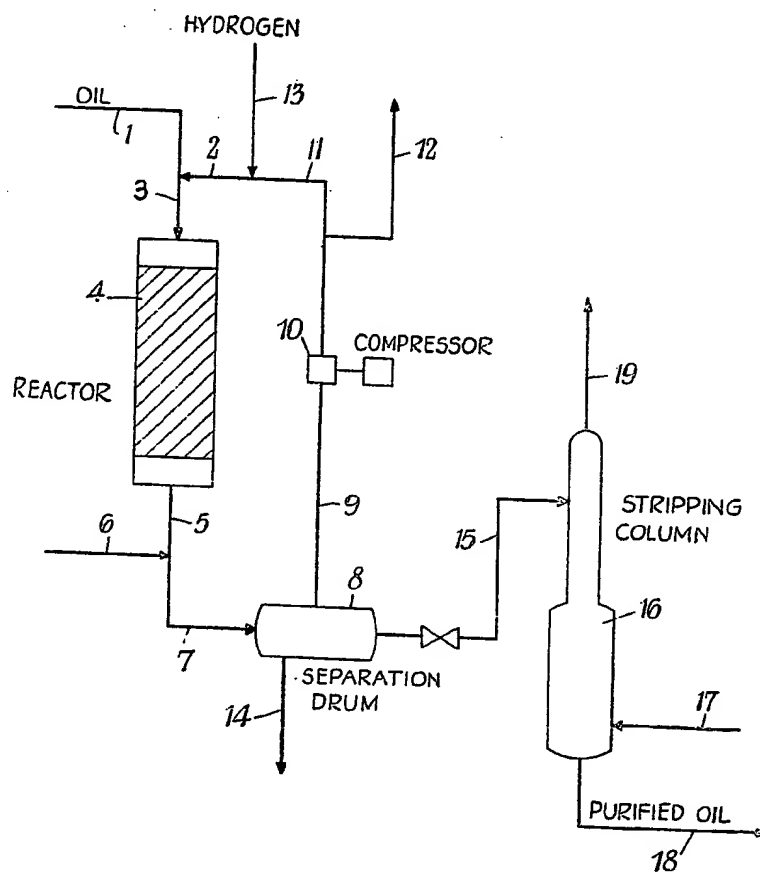
- removal of more than 99.9% of the contaminating nitrogen-containing compounds from a non-refractory hydrocarbon middle distillate boiling up to about 600°F., which process comprises contacting said distillate at 550 to 750°F. together with excess hydrogen at a pressure of 500 to 1500 psig and at a liquid hourly space velocity of 0.5 to 5. 30
14. A process according to Claim 6 for the removal of more than 99.9% of the contaminating nitrogen-containing compounds from a refractory hydrocarbon gas oil boiling up to about 750°F., which process comprises contacting said gas oil at 650 to 800°F. together with excess hydrogen at a pressure of 500 to 2500 psig and at a liquid hourly space velocity of 0.2 to 5. 35
15. A process according to Claim 6 for the removal of more than 99% of the contaminating nitrogen-containing compounds from a high boiling hydrocarbon oil boiling up to about 860°F., which process comprises contacting said oil at a temperature of from 600 to 800°F. together with excess hydrogen at a pressure of 500 to 4000 psig and at a liquid hourly space velocity of 0.2 to 5. 40
16. A process according to Claim 6 for the removal of more than 80% of the contaminating nitrogen-containing compounds from a heavy hydrocarbon distillate boiling up to about 1050°F., which process comprises contacting said distillate at a temperature of from 600 to 800°F. together with excess hydrogen at a pressure of 500 to 4000 psig and at a liquid hourly space velocity of 0.2 to 10. 45
17. A process for the catalytic hydrodenitrication of a distillable hydrocarbon oil, substantially as hereinbefore described with reference to the accompanying drawing. 50
18. A process for the catalytic hydrodenitrication of a distilled hydrocarbon oil, substantially as described in Example 3 of the foregoing Examples.
19. Distillable hydrocarbon oils, whenever catalytically hydrodenitrified by the process claimed in any one of Claims 6, 7, 9 and 11 to 18.
20. Distillable hydrocarbon oils, whenever catalytically hydrodenitrified by the process claimed in Claim 8 or 10.

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